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(Unclassified Title)

ANNUAL SUMMARY REPORT, INORGANIC HALOGEN OXIDIZERS

(29 May 1964 through 28 May 1965)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency
Washington 25, D. C.
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FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 May 1964 through 28 May 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist of the Fluorine Chemistry Unit, as the Responsible Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, Dr. C. J. Schack, and Mr. R. D. Wilson. Dr. C. B. Lindahl joined the technical staff during the last two months.

ABSTRACT

The new oxidizer oxychlorine trifluoride, ClF_3O, has been prepared in high yields by the fluorination of Cl_2O. Preliminary results indicate this new oxidizer boils at 30 ±5 C.

Concomitant with the formation of ClF_3O, it was found that Cl_2O is acidic to CsF inasmuch as complexes of the type $CsF \cdot Cl_2O$ are formed. This material represents a new class of compounds.

The preparation of ClF_3O was attempted by a variety of routes. Metathetical reactions of ClF_5 did not yield ClF_3O nor did the careful hydrolysis of ClF_5 give rise to ClF_3O. The fluorination of commercial calcium hypochlorite gave inconclusive results. Discharge reactions of F_2 with Cl_2O and ClO_2 gave no new species; nor did the discharge reaction of O_2 with ClF_3 and ClF_5 give rise to new compounds.

The preparation of Br_2O was accomplished for study with F_2 and CsF. The compound $(IF_3O)_x$ was found to be best represented by the composition $IO_2^+IF_6^-$.

Using HNF_2 and ClF_3 in a variety of forms failed to yield ClF_2NF_2. The stoichiometry of the reaction was fo·.d to follow the equation

$$ClF_3 + 3HNF_2 \longrightarrow ClNF_2 + N_2F_4 + 3HF$$

It was also found that the action of ClF on HNF_2 gave a quantitative yield of $ClNF_2$ and represents a new preparation of $ClNF_2$.

The reaction of NF_3O and BF_2Cl failed to give NF_2ClO.

The F^{19} n.m.r. examination of the systems $FNO\text{-}ClF_5$ and $FNO_2\text{-}ClF_5$ showed no interaction in the liquid state.

(Confidential Abstract)

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INTRODUCTION

This report presents the approaches taken during the past year in seeking new high-energy oxidizers. As will be seen, a variety of techniques were employed in attempts to achieve this goal. Because of the high potential of species such as ClF_xO, much of the effort was directed toward the pursuit of either ClF_3O or ClF_5O. Partial success was realized in that ClF_3O was synthesized; preliminary data are presented.

In addition to extensive work on both ClF_xO species and studies in the IF_3O system, this report also presents the rationale and results of the condensation reactions of HNF_2 and interhalogen fluorides. This reaction system has long awaited a more complete elucidation.

DISCUSSION

OXYCHLORINE TRIFLUORIDE (ClF_3O)

The studies of ClF_3O can be grouped into three categories: (1) direct fluorination of chlorine (I) oxides, (2) discharge reactions of chlorine fluorides, and (3) metathetical reactions of chlorine (V) fluoride. Success was achieved using only the direct fluorination approach.

The preparation of ClF_3O was accomplished readily by the action of F_2 on Cl_2O (this will be discussed later). The characterization of ClF_3O is not yet complete but enough data have been obtained to infer the composition ClF_3O. Oxychlorine trifluoride is a water-white liquid and freezes to a white solid. Some preliminary physical characteristics are shown in Table 1.

TABLE 1

PROPERTIES OF ClF_3O

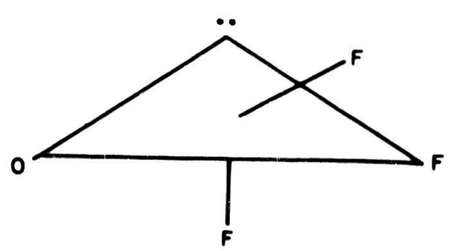
Melting Point, C	-68 ±3
Boiling Point, C	+30 ±5
Molecular Weight	
Found (vapor density)	101
Calculated	108.5

Inconsistent elemental analyses were obtained, however, by the preliminary reduction of ClF_3O with anhydrous NH_3 and the subsequent analysis for Cl^- and F^-. The average F/Cl ratio in three different samples was slightly

greater than 3 (3.2); however, material balances were not good. It is believed that the principal errors are introduced in the (1) volume measurement of ClF_3O, (2) partial reaction in transferring, and (3) possible presence of ClO_4^- and/or ClO_3^- in the final solutions. For example, it was found that it readily gives $FClO_2$. Future reductions are contemplated with Hg as in the following equations:

$$4Hg + 2ClF_3O \longrightarrow HgCl_2 + 3HgF_2 + O_2$$

The infrared trace of ClF_3O is shown in Fig. 1. A spectrum using an IR-7 was measured, and bands were found at 1220 cm^{-1}, 680 cm^{-1}, 490 cm^{-1}, 320 cm^{-1}, and 286 cm^{-1}. While it is not possible to assign the bands without also measuring the Raman effect, the spectrum permits us to say the compound ClF_3O does not have the CH_3F structure, but probably possesses C_s symmetry. The C_s symmetry is best represented by a trigonal bipyramid with two apical fluorine atoms and the three equatorial positions being occupied by an electron pair, the oxygen atom and the unique fluorine:



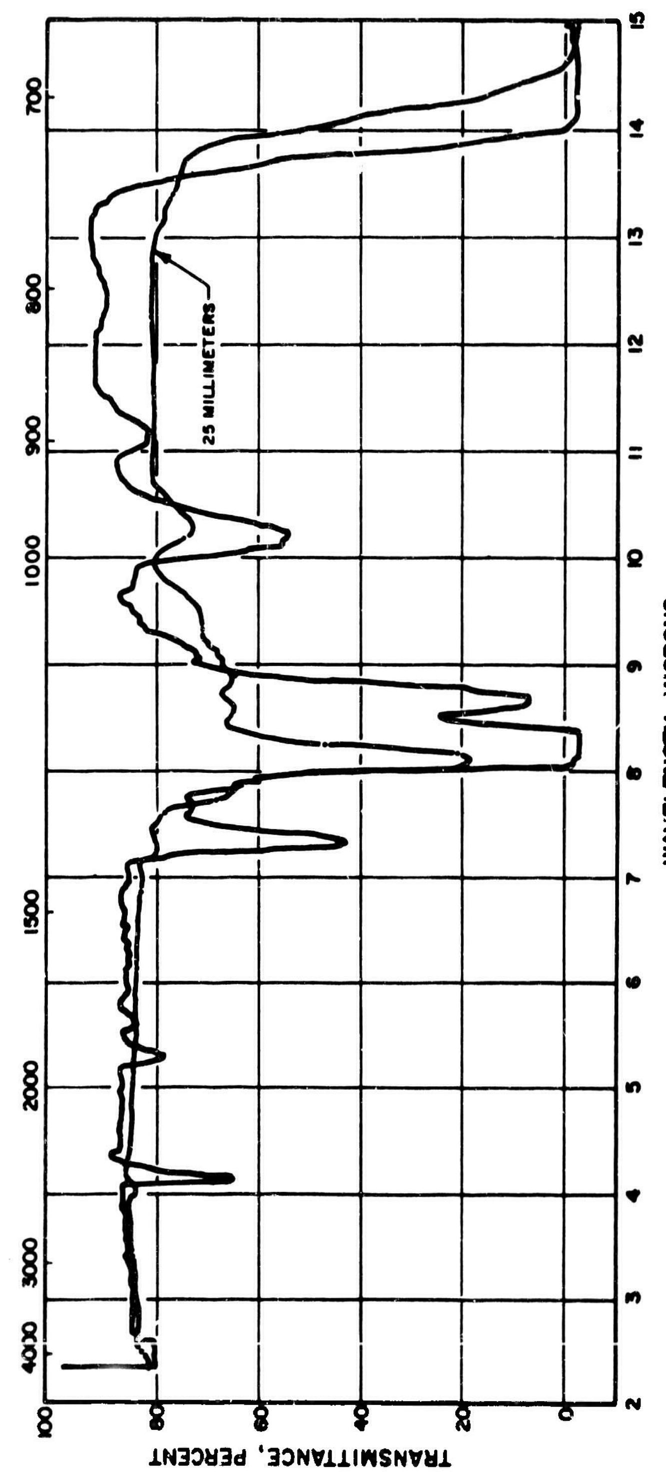


Figure 1. Infrared Spectra of ClF_3O

The proposed structure of ClF_3O is somewhat analogous to the structures of both ClF_3 and SF_4 (Ref. 1 and 2). Such a structure should give rise to a F^{19} n.m.r. spectrum consisting of a doublet and a triplet in the ratio 2:1. The spectra obtained for the pure material as well as solutions in chlorine and Freon-11 show, however, only a single resonance for ClF_3O (Table 2).

TABLE 2

F^{19} NMR DATA FOR ClF_3O

Sample	Chemical Shift Relative to F_2, ppm	Assignment	Temperature, C
Cl_2 Solution (impure)	141 broad	ClF_3O	-60
	167 doublet	ClF_5	
	373	?	
	397	?	
Freon-11 Solution 12 m/o	141 singlet	ClF_3O	-88
	414	$CFCl_3$	
Neat Liquid	161 singlet	ClF_3O	-65
	165 singlet	ClF_3O	25
	156 collapsed	$ClF_3O_{(s)}$	-71

The failure to observe two distinct types of fluorine, even at -88 C, may be attributed either to exchange or to truly equivalent fluorines, as in a structure with C_{3v} symmetry (Ref. 3). This latter possibility may be excluded on the basis of the infrared data for ClF_3O.

Low-temperature exchange on the other hand, also has been observed for a similar compound, SF_4, especially in the presence of trace impurities (Ref. 4). Splitting of the ClF_3O resonance was observed between -65 and -71 C when the pure material was examined. This appeared to be due to partial liquid entrapment in solid ClF_3O, since the relative peak intensities were very temperature-dependent, and complete collapse of the structure, indicating freezing, occurred at -68 ±3 C. This premise was substantiated when no splitting or freezing occurred in a Freon-11 solution of ClF_3O at -88 C. The marked downfield solvent shift of 20 ppm suggested that ClF_3O was somewhat associated in the pure liquid, as was also indicated by its extrapolated normal boiling point of 30 ±5 C.

A sample of ClF_3O in Cl_2 was run in a Kel-F n.m.r. tube with known impurities, $FClO_2$ and ClF_3, present. In addition, ClF_5 used to passivate the tube, was also present. The absence of the expected $FClO_2$ or ClF_3 lines and the width of the observed ClF_3O resonance further attested to the likelihood of exchange involving ClF_3O. Unassigned singlet resonances at 373 and 397 ppm in the ratio 2:1 may have been due to ClF_3 or CF compounds arising from reaction with the Kel-F tube. Quartz n.m.r. tubes were used for the other ClF_3O samples without observing impurities such as SiF_4.

On the basis of the relative areas for the ClF_3O and $CFCl_3F^{19}$ resonances in a 12 m/o solution of ClF_3O, a ratio of 2.8 fluorines per molecule was calculated.

Fluorinations

The selection of starting materials for fluorination to ClF_3O and subsequently ClF_5O was restricted to chlorine (I) species; i.e., $Ca(OCl)_2$ (commercial), Cl_2O and $ClO{\cdot}AsF_5$. The first of these, $Ca(OCl)_2$, was tested with F_2 at 125 C and ambient temperature, and subsequently at -80 C with CsF. No new products were noted in all these experiments, with $FClO_3$, $FClO_2$, Cl_2O_6 and ClO_2 being identified. Considering the extreme reactivity of ClF_3O, it is not surprising that it was not observed in the fluorination of commercial calcium hypochlorite. Bunn (Ref. 5) has stated that X-ray examination of available material indicated a high $Ca(OH)_2$ content. By analogy to ClF_5 and ClF_3, $Ca(OH)_2$ and ClF_3O are not expected to be compatible.

The use of Cl_2O offered more hope because good control could be exerted over reactant purity. Fluorine and Cl_2O were examined at 125 C, at ambient temperature, and at -80 C. As yet, ClF_3O has been formed only at the lower temperatures. Very low yields are obtained using neat Cl_2O and F_2. However, if the Cl_2O is complexed with an alkali metal fluoride, the subsequent fluorination gives ClF_3O in yields consistently over 70 percent.

The only complex of Cl_2O fluorinated thus far is that formed with CsF. Marked vapor pressure lowering of Cl_2O on CsF has been observed up to 0 C. In fact, the complex formed is colorless (or white) with the blood red color of Cl_2O being completely discharged. Upon warming to ambient temperature, however, the addition compound slowly dissociates reversibly in the vacuum line to Cl_2O.

In view of the above data, we are proposing that CsF adds to Cl_2O as in the equation:

$$xCsF + Cl_2O \longrightarrow Cs_xCl_2F_xO \quad x = 1 \text{ and/or } 2$$

It is also proposed that the Cl_2O structure is intact in the suggested anions $FClOCl^-$ and $FClOClF^=$. Experimental verifications of these hypotheses are in progress.

Metathetical Reactions of ClF_5

Partial hydrolysis of ClF_5 to ClF_3O has been unsuccessful in the past. Instead, $FClO_2$ was formed, indicating perhaps that ClF_3O is more reactive with water than is ClF_5 (Ref. 27). Less reactive conditions with a variety of oxygen sources were examined in a series of metathetical reactions. Arsenic pentafluoride was often used to promote the reaction of ClF_5 as cationic ClF_4^+ with oxygen-containing materials. In no case was there evidence of ClF_3O formation or intermediates leading to it.

(1) $ClF_5 \cdot AsF_5 + H_2O(s) \xrightarrow{0\ C} ClF_5,\ HF,\ AsF_3O$

(2) $ClF_5 \cdot AsF_5 + (CF_3CO)_2O \xrightarrow{0\ C}$ vigorous reaction, apparatus rupture

(3) $ClF_5 \cdot AsF_5 + N_2O_3 \xrightarrow{-23\ C} (NO^+AsF_6^-),\ {}^*NO_2^+AsF_6^-,\ Cl_2$

(4) ClF_5 (diluted with N_2) + HgO (yellow) $\xrightarrow{0\ C} FClO_2$

(5) $ClF_5 \cdot AsF_5 + KNO_3 \xrightarrow{25\ C} ClF_5,\ (K^+AsF_5NO_3^-)^*$

(6) $ClF_5 \cdot AsF_5 + KNO_3 + HF \xrightarrow{25\ C} KHF_2,\ NO_2^+AsF_6^-,\ ClO_2,\ FClO_2,\ FClO_3$

(7) $ClF_5 + KNO_3 + HF \xrightarrow{25\ C} FNO_2,\ ClO_2,\ FClO_2,\ FClO_3$

(8) $ClF_5 + KClO_4 \xrightarrow{150\ C}$ No reaction

(9) $ClF_5 + KClO_4 + HF \xrightarrow{25\ C} KHF_2,\ ClO_2,\ FClO_2,\ FClO_3$

*Solid products in parentheses were not identified but deduced from a material balance.

The reaction of ClF_5 with KNO_3 and $KClO_4$ was promoted by the addition of HF, probably through nitric and perchloric acid formation. Arsenic pentafluoride reacted with the bases H_2O and NO_3^- more readily than did ClF_5; consequently little promise is held for the formation of ClF_3O by metathesis on the basis of the above reactions.

The synthesis of ClF_3O was also attempted by the oxidation of ClF_3 by ozone.

$$ClF_3 + O_3 \xrightarrow{?} ClF_3O + O_2$$

The only reaction observed was the combined attack of ClF_3 and O_3 on the Kel-F infrared cell in which the reaction was run. This was deduced from the observation that only CF materials were formed.

Discharge Reactions

However limited the use of the electric discharge may appear when used in a "conventional" manner, the fact remains that the ternary system N_2-F_2-O_2 does give products containing all three elements, i.e., NF_3O. The question immediately arose as to whether ClF_3O and ClF_5O can result from the ternary mixture Cl_2-F_2-O_2. This obvious analogy was tested by subjecting this mixture to a discharge at -80 C. No new compounds were observed using a F_2-Cl_2-O_2 ratio of 6:1:1. Products found were ClO_2, $FClO_2$, ClF_3, and ClF_5. Due to the accidental presence of air in the starting material, NO_2, FNO, FNO_2, and $ClONO_2$ also were formed. Additional experiments were carried out at -196 C, and in addition to the above products, Compound B (Ref. 6) was found. This compound was identified as WF_6 which arose from the attack by F_2 on the tungsten used to achieve the glass-to-metal seals in the discharge apparatus. These results are consistent with those previously obtained in the Rocketdyne laboratories in discharge reactions of Cl_2 and F_2 where O_2 was known, at times, to be an impurity.

Subjecting mixtures of Cl_2, F_2, and O_2 to the electric discharge does not appear to be promising using the technique described above. It appeared that variations in the discharge technique may offer more versatility in product control than the techniques now employed. One method decided upon was to utilize a gas-solid reaction where the gas is some excited species such as F_2* or O_2*. The solid substrate is in essence a cold wall where excess energy can be readily dissipated. The essential difference from the previous experiments is that specific bond formation is sought by the interaction of an excited species with a readily oxidized material as opposed to an overall excitation followed by random and fortuitous

recombinations. The following equations demonstrate the reactions considered:

$$ClF_3 + O^* \longrightarrow ClF_3O^* \longrightarrow ClF_3O + Q$$

$$ClF_5 + O^* \longrightarrow ClF_5O^* \longrightarrow ClF_5O + Q$$

$$FClO_2 + F^* \longrightarrow ClF_3O_2^* \longrightarrow ClF_3O_2 + Q$$

$$Cl_2O + F^* \longrightarrow ClF_2OClF_2^* \longrightarrow ClF_2OClF_2 + Q \begin{cases} \nearrow ClF_3 + FClO \\ \searrow ClF + ClF_3O \end{cases}$$

$$Cl_2O + F^* \longrightarrow ClF_4OClF_4^* \longrightarrow ClF_4OClF_4 + Q$$

$$ClF_4OClF_4 \longrightarrow ClF_3 + ClF_5O$$

Thus, either O_2 or F_2 can be considered for the above oxidations, depending on the choice of the starting material.

The advantages of the solid-gas reaction at once became obvious for several reasons. First, it can be predicted that a higher degree of control can be exerted with regard to the structure of the products. This is dictated by the fact that one of the reactants, the solid, is the wall at which immediate dissipation of excess energy is anticipated. This is particularly important when it is realized that wall reactions enhance product formation in a discharge reaction. Concomitantly, another feature is suggested in that higher yields of complex moieties may be realized. It should be recalled (Ref. 7) that in the discharge preparation of NF_3O from various gas mixtures the same low yields were obtained for the starting material combinations NF_3-O_2, N_2-O_2-F_2, and N_2-OF_2. This is no doubt based upon the statistical nature of a favorable combination of the excited F, N, and O to give the desired product.

To test the above assumptions, a model reaction was selected for study at -196 C. The desired reaction was:

$$FNO + F^* \longrightarrow F_3NO^* \longrightarrow F_3NO + Q$$

The use of FNO was selected because it not only has an oxidizable "central" atom but it should give the known compound NF_3O. The apparatus used was a U-shaped Pyrex discharge tube connected to a glass U-trap. Both were maintained at -196 C, and a constriction was placed in the trap about 10 inches downstream from the discharge zone. Nitrosyl fluoride was then condensed at the constriction, and F_2 was introduced into the discharge tube at a pressure below 50 millimeters.

Examination of the products in the trap showed NF_3O to be present, representing a 5-percent conversion of the FNO. A separate experiment, a control without FNO, yielded no NF_3O in the trap. The control was carried out in view of the fact that the F_2 supply often is contaminated with small amounts of air. Subsequent experiments showed the FNO (s)-F* reaction to be reproducible. In view of the moderate success with the model selected, it appeared desirable to extend it to halogen oxides.

The selection of reactants in seeking routes to new F Cl, and O species is quite limited. Prime consideration should be given to the valence of the "central" atom. On this basis, then, all chlorine (VII) species do not appear to be desirable since neither oxidations can occur nor is the replacement of O on chlorine probable. Consequently, perchloryl fluoride does not appear to be a suitable precursor for discharge studies. The chlorine compounds which meet the imposed requirements are $FClO_2$

(or ClO_2) and Cl_2O. Each can be envisioned as giving rise directly to the sought oxychlorofluorides:

$$Cl_2O \longrightarrow ClO\cdot + 1/2\ Cl_2$$

$$F\cdot + ClO\cdot \longrightarrow FClO$$

$$FClO + F_2 \longrightarrow ClF_3O$$

The reaction of Cl_2O as written proceeds through the rupture of a ClO bond which requires little energy in Cl_2O. The photodecomposition of chlorine monoxide proceeds initially according to the first step of the equation $Cl_2O \longrightarrow ClO\cdot + 1/2\ Cl_2$, as does the chlorine-atom sensitized decomposition (Ref. 3).

To extend fluorination to halogen oxides, the selected precursors were subjected to conditions similar to those in the FNO(s)-F* experiments. For example, chlorine monoxide was frozen at -196 C on the reactor wall just downstream from the glow discharge electrodes. Fluorine passing between the electrodes is converted to fluorine atoms. These radicals are then able to bombard the solid reactant and effect fluorination.

By maintaining starting materials and products at -196 C, side reactions are minimized and hence the possibility of conversion to new energetic species is maximized.

In extending the solid-gas reaction to chlorine systems, two electrical discharge tubes have been employed. The first design maintained the Cl-O compound to be attacked at -196 C but left the electrodes above the bath where they were cooled by an air blower.

Chlorine monoxide was reacted twice with essentially the same result. All of the Cl_2O was used up, but the only ClO species formed was ClO_2. Also formed were Cl_2 and much SiF_4. The chlorine dioxide and chlorine probably arose directly from the decomposition of Cl_2O.

$$Cl_2O \longrightarrow ClO\cdot + Cl\cdot$$

$$ClO + Cl_2O \longrightarrow ClO_2 + 2Cl\cdot$$

Initiation of this sequence by F atoms comparable to the known Cl atom process is possible. A chain radical reaction promoted by the product Cl atoms makes fluorine necessary only for initiation and not propagation. Thus, small amounts of ClF could have been formed but not detected.

Air contamination in one run was noted by the production of a small quantity of chlorine nitrate. This again is a well-characterized product of ClO radical reactions (Ref. 8):

$$ClO\cdot + NO_2\cdot \longrightarrow ClNO_3$$

Due to difficulties with the method originally selected for the preparation of $FClO_2$, ClO_2 was present as an impurity. Nevertheless, since ClO_2 is the precursor of $FClO_2$ it was expected that it would not adversely affect the reaction. In fact, fluorination of ClO_2 would itself indicate that suitable fluorination conditions were being approached.

Using this mixture in the solid phase, it was found that the discharge reaction resulted in consumption of the $FClO_2$ but not of the ClO_2. The products were $FClO_3$ and SiF_4, in addition to the ClO_2. The conversion of chloryl fluoride to perchloryl fluoride is certainly not the result of fluorination, and the failure of the ClO_2 to be fluorinated leads to the conclusion that fluorination conditions were lacking.

The formation of appreciable amounts of SiF_4 using this technique can account for the findings. The activated fluorine may react with the glass of the tube around the electrodes too fast to allow sufficient amounts to reach the intended reaction zone. In addition, oxygen that is liberated by the conversion of the silica to SiF_4 may be responsible for the oxidation of $FClO_2$ to $FClO_3$.

So severe was the etching of the apparatus near the electrodes and the thermal strain encountered during operation, that the discharge tube cracked after several experiments. A newly designed system was fabricated in which both electrodes and substrates could be immersed in a liquid nitrogen bath. This tube showed only limited etching after several experiments.

Again utilizing Cl_2O as the starting material, three experiments were conducted. Two distinct results were obtained, depending upon the purity of the fluorine. In the absence of air impurity, most of the chlorine monoxide was reacted after 20 minutes. The yield of $FClO_2$, ClO_2, and ClF_5, along with a trace of SiF_4, demonstrated that fluorination had been effected.

When air-contaminated fluorine passed through the discharge, the product composition was altered. As expected, ClO_2 and trace amounts of SiF_4 were formed. However, no $FClO_2$ was observed. Furthermore, appreciable yields of $ClNO_3$, ClF_5, and NF_3 were noted. These molecules are all known to result from the glow discharge reaction of the appropriate elements. The important point derived from the experiment is that fluorination of Cl in Cl=O bonds is much more difficult to achieve than is the corresponding fluorination of the other atoms or groups.

Although purely hypothetical, the following reaction scheme indicates some of the possible intermediate hypofluorites and shows how they might give rise to ClF_5:

$$FClO_2 + F_2 \xrightarrow{\text{discharge}} [F_2ClO(OF)]$$

$$[F_2ClO(OF)] + F_2 \xrightarrow{\text{discharge}} [F_3Cl(OF)_2]$$

$$[F_3Cl(OF)_2] \longrightarrow ClF_5 + O_2$$

$$2\ [F_3Cl(OF)_2] \longrightarrow ClF_5 + FClO_2 + O_2 + 2\ F_2$$

Since no ClF_3 was found, it is probably not involved in the conversion of $FClO_2$ to ClF_5. The absence of ClF_3 also precludes Cl_2 as an intermediate. In discharge reactions of F_2 and Cl_2, the ratio of ClF_3 to ClF_5 was always found on the order of 10 to 1.

To determine the generality of displacing oxygen from XO_2 species by discharge fluorination, this reaction was carried out with sulfur dioxide. If any hypofluorites of sulfur are formed, they should be stable to warming (e.g., SF_5OF), and thus the intermediate character of Cl-OF species in the overall reaction could be demonstrated. Under the same conditions employed with $FClO_2$, it was determined that SO_2F_2 and SF_6 were produced. Thus, fluorination and displacement did occur, but intermediate OF species were not isolated.

The reaction of ClF_5 in a discharge at -80 C was examined. It was hoped that ClF_2 or ClF_4 radicals might be generated. Such radicals might react with the glass reactor to form new F-Cl-O compounds or couple to yield compounds such as $(F_4Cl)_2$. The coupling reaction is analogous to the preparation of B_2Cl_4 in a mercury electrode discharge apparatus (Ref. 28).

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In a series of experiments beginning at the lowest voltage at which a discharge could be maintained and then at higher voltages, it was determined that no new species were obtained. At the lower voltages, the ClF_5 was essentially unchanged. At higher voltages, the ClF_5 was completely destroyed, giving mainly F_2 and Cl_2. The other products were ClO_2, $FClO_2$, and SiF_4.

The discharge reactions reported have indicated several areas in which new metastable compounds may have been produced. The formation of noncondensible gases during product workup may be indicative of the presence of O_2F_2. However, the characteristic color of O_2F_2 was never observed in any of the reaction mixtures.

OTHER OXYHALOGEN TRIFLUORIDES

It appears highly probable that ClF_3O is the first example of an interhalogen oxyfluoride of molecular composition XF_3O. The existence of an iodine compound of that empirical composition has been known for some time (Ref. 9). However, examination of the chemical and physical properties of this material makes it most unlikely that the empirical composition is the same as the molecular composition. For example, IF_3O is a solid which does not melt to 110 C but decomposes according to the following equation:

$$2IOF_3 \longrightarrow FIO_2 + IF_5$$

This non-melting characteristic and reasonably high decomposition temperature are, for the simple IF_3O molecule, extremely unlikely, especially in view of the fact that IF_5O (of proven molecular composition) has a melting point of +4.5 C (Ref. 10). It seems more probable that the material is actually $IO_2^+IF_6^-$, as has been speculated previously (Ref. 9). Attempts to prepare and isolate IF_3O for characterization have been only partially successful. The reactions tried were:

$$I_2O_5 + 3IF_5 \longrightarrow 5IF_3O$$

$$IF_5 + H_2O \longrightarrow IF_3O + 2HF$$

The isolated samples have been of low fluorine content. Two problems are apparently being encountered in the first method. First of all, there has not been complete reaction of the I_2O_5, despite the use of IF_5 in excess of that originally reported; secondly, on work up of the solid products, the excess IF_5 has been pumped off while heating at 50 to 60 C. This temperature may be too high, and may result in the decomposition of IF_3O. The observed fluorine contents (5 to 6.5 percent) can only be explained on this basis.

The F^{19} n.m.r. spectra of I_2O_5 in IF_5 at ambient and elevated temperatures and also that of possible related species KIF_6 and KIF_4 in IF_5 (prepared according to Ref. 11 and 12) were run. Iodine pentafluoride alone showed no fluorine exchange from room temperature through +80 C. However, I_2O_5 in IF_5, when heated to form IF_3O, showed only a single slightly broadened, band at +405 ppm, indicating complete exchange with the solvent. At room temperature, where the IF_3O is only slightly soluble in IF_5, the solvent exchange stopped, and there remained only one singlet peak at +405 ppm. This singlet is comparable to that of KIF_6 in IF_5 at +404 ppm, and lends

credence to the composition $IO_2^+IF_6^-$ for IF_3O. No evidence for other F^{19} absorptions was found. The spectrum of KIF_4 in IF_5 showed only collapse of the multiplet structure of the solvent, indicating slow fluorine exchange; this was different than either the supposed IF_3O or KIF_6.

The isolation of $(IF_3O)_2$ of good purity will enable us to conduct infrared characterization experiments and perhaps give conclusive proof of the composition of the material.

The preparation of BrF_3O has not been reported. However, the known existence of a suitable precursor, Br_2O, to that used in the formation of ClF_3O, namely Cl_2O, makes the synthesis of BrF_3O and BrF_5O appear feasible. The production of Br_2O in the same manner as Cl_2O, using yellow HgO and Br_2 with nitrogen carrier gas, was unsuccessful. The preparation of this material in $CFCl_3$ solution at low temperature (-23 C) was carried out. While not yet completely freed of Br_2, a brown-black solid believed to be Br_2O has been observed. Furthermore, vapor phase chromatography of a partially decomposed sample has shown that Br_2 and O_2 are the only products present. While a pure Br_2O sample might be desirable, it is not necessary since it will be necessary to use the compound in solution to form the CsF complex prior to fluorination. Bromine contamination should not affect this complex formation. Also, this proposed synthesis of BrF_3O may be simplified by the formation of the CsF complex <u>in situ</u> as the Br_2O is being generated. Experiments utilizing both these routes are planned.

DIOXYHALOGEN TRIFLUORIDES

Several attempts have been made to prepare FIO_2 and $FBrO_2$ for use as intermediates in catalytic fluorinations. It is expected that these materials would lead to the new compounds IF_3O_2 and BrF_3O_2. In this way it is hoped that information regarding the feasibility of similar fluorinations of $FClO_2$ will be acquired.

The preparation of FIO_2 has been unsuccessful via the following reaction (Ref. 13):

$$I_2O_5 + F_2 \longrightarrow 2FIO_2 + 1/2\ O_2$$

It has not been possible to completely remove the solvent from the product. Syntheses of this compound will be attempted by the thermal decomposition of IF_3O (Ref. 9) as this becomes available.

The preparation of $FBrO_2$ from $KBrO_3$ and BrF_5 (Ref. 14) has been hampered by the low purity BrF_5 available. Substitution of ClF_5 as a reactant was unsuccessful. When pure BrF_5 is obtained, this procedure will be tried again.

DIFLUORAMINO DERIVATIVES OF CHLORINE FLUORIDES

A series of studies was conducted employing difluoramine and other inorganic moieties to achieve the synthesis of new $-NF_2$ containing inorganic oxidizers. A primary effort was directed to the preparation of F_xClNF_2 compounds. It should be recalled that products of this type were sought some time ago (Ref. 24). In the cited work, NF_3O was first produced due to ClO_2 impurities. For the present work, extremely high purity ClF_3 was used.

The Reaction of Difluoramine and Chlorine Trifluoride

The amphoteric character of both difluoramine (Ref. 15 and 16) and chlorine trifluoride (Ref. 17 and 18) has been well established. Utilization of this acid-base property was attempted in an effort to achieve a condensation reaction between these materials.

$$ClF_3 + HNF_2 \xrightarrow{?} F_2ClNF_2 + HF$$

It was determined that the reaction proceeds rapidly and smoothly to yield chlorodifluoramine and tetrafluorohydrazine as follows:

$$ClF_3 + 3HNF_2 \longrightarrow ClNF_2 + N_2F_4 + 3HF$$

Despite attempts at limiting the amount of available difluoramine, it was not possible to isolate the simple condensation product, F_2ClNF_2. When equimolar or excess amounts of chlorine trifluoride were employed, it was found that chlorodifluoramine was the principal product (yields up to 95 percent based on the limiting reagent). Thus the establishment of a Cl-N bond is a primary occurrence. However, the substitution of the NF_2 group on chlorine apparently increases the reactivity of the remaining fluorine atoms in the molecule markedly. This results in their subsequent reaction with more difluoramine or the surfaces of the reaction vessel.

Since the reaction of chlorine and difluoramine to form chlorodifluoramine is known (Ref. 19) to be slow, the failure to find chlorine as a product regardless of the reactant stoichiometry shows that a straightforward reduction of the ClF_3 to Cl_2 does not occur.

It was also independently established that chlorine monofluoride and difluoramine react in equimolar quantities to form chlorodifluoramine.

$$ClF + HNF_2 \longrightarrow ClNF_2 + HF$$

This reaction is also not accompanied by any reduction to chlorine.

Two routes to the formation of $ClNF_2$ can be considered. They are visualized in the following sequences:

a. $ClF_3 + HNF_2 \longrightarrow ClF_2NF_2 + HF$

b. $ClF_2NF_2 + 2HNF_2 \longrightarrow ClNF_2 + N_2F_4 + 2HF$

a'. $ClF_3 + 2HNF_2 \longrightarrow ClF + 2HF + N_2F_4$

b'. $ClF + HNF_2 \longrightarrow ClNF_2 + HF$

It was tempting to choose the condensation shown in (a) as being the initial step with the subsequent reduction of the condensation product, ClF_2NF_2. However, due to the experimentally confirmed reaction (b') it appears that the primary process is probably the reduction of ClF_3 by HNF_2.

Additional Difluoramine-Chlorine Fluoride Systems

After repeated attempts with varying stiochiometries of chlorine trifluoride and difluoramine failed to yield F_2ClNF_2, several other variations in the form of the reactants were utilized. In particular, $ClF_2^+BF_4^-$, $KF \cdot KClF_4$, and $RbClF_4$, complexes of ClF_3, were used. In some instances a $HNF_2 \cdot BF_3$ complex was employed.

The reaction of neat ClF_3 and HNF_2 was found to be very rapid, even instantaneous. Therefore, BF_3 was used to complex either ClF_3 or HNF_2, both to slow down the reaction and also to prevent subsequent reaction of the remaining Cl-F bonds. The desired moderation in the reaction rate was achieved. For example, at -80 C, when equimolar amounts of ClF_3 and $HNF_2 \cdot BF_3$ were mixed, the appearance of $ClNF_2$ and other N-F species was still noted after 4 days, although most of the total yield was obtained after 40 minutes. This pronounced decrease in the rate of the reaction is probably caused by the complexing of ClF_3 by the BF_3 made available by reaction of HNF_2, as well as the decrease in free HNF_2 concentration.

Chlorodifluoramine was the principal nitrogen-containing product in these BF_3 systems whether 1:1, 1:2, or 2:1 molar proportions of ClF_3 and HNF_2 were used. The results of these experiments also showed that reaction temperatures above -80 C led to an increased proportion of N_2F_4 among the products. The relative amount of N_2F_4 was also increased by an excess of ClF_3. Nitrogen trifluoride was found only in trace amounts at or below -80 C, or when there was no excess of Cl-F reagent.

The solid compounds $KF \cdot KClF_4$ and $RbClF_4$ were treated with pure HNF_2 and it was determined that reaction at -80 C was very slow. The rubidium salt was the least reactive of the Cl-F species tested. Conclusions regarding the reactivity of the potassium salt are difficult to make, since in one experiment an explosion occurred upon warming the mixture directly to room temperature from -142 C. However, when the intermediate temperature of -80 C was maintained for some time before further warming, no explosion resulted.

The yields of $ClNF_2$ obtained with these solid Cl-F compounds were approximately 50 percent or lower. The larger amounts of N_2F_4 found probably reflect the higher temperature needed to achieve reaction. The formation of N_2F_4 is increased, then, by increased temperature as well as by the absence of ClF_3 complexing moieties.

The RbF and KF formed or present initially in these reactions proved effective in scavenging the HF obtained during the reactions. To have the greater reactivity of the volatile ClF_3 and yet still eliminate the possible detrimental effects of free HF, some reactions were conducted using NaF to "neutralize" the HF. The results were not significantly different than those found in experiments run in the absence of NaF.

Recovery of Nitrogen-Containing Products. In those reactions conducted using Pyrex glass apparatus and BF_3 as a complexing agent, the complete recovery of difluoramine nitrogen as volatile compounds was not realized. The remaining 10 to 20 percent was probably present in a residual white solid. Upon hydrolysis, these solids gave off NO_2, indicating the presence of either $NOBF_4$ or NO_2BF_4. This solid did not contain Cl-N-F compounds since all of the reactant chlorine was obtained in the volatile materials.

Elimination of the glass side reactions was achieved by the use of an all Kel-F and Teflon reactor. However, both the neat and complexed reactants still gave essentially the same basic results with this apparatus. In this instance all the nitrogen of difluoramine was recovered in the form of volatile N-F compounds. Moreover, a better recovery of unreacted ClF_3 was possible.

Difluoramine-Chlorine Pentafluoride Systems. Chlorine pentafluoride and difluoramine were reacted in metal-Teflon, Pyrex, and Kel-F-Teflon reactors. As with chlorine trifluoride, the pentafluoride reacted with difluoramine to give mixtures of $ClNF_2$, N_2F_4 and NF_3. Unlike ClF_3, however, a smooth reaction at -80 C gave products which were more sensitive to the glass environment. Within minutes, the formation of NO_2 could be visibly detected. If not fractionated at once, practically no N-F or Cl-F materials were found. Instead, the degradation products NO_2, HNO_3, Cl_2, ClO_2 and $FClO_3$ were obtained. Rapid fractionation of an equimolar mixture yielded as much as 77 percent $ClNF_2$ with 23 percent recovery of ClF_5. The remaining HNF_2 was converted to N_2F_4 and NF_3. In the Kel-F-Teflon reactor, a good correspondence between the amount of $ClNF_2$ formed and the amount of ClF_5 reacted was also found. The presence of the side products N_2F_4 and NF_3 again indicated a high reactivity of the Cl-F bonds of the original intermediates.

Factors Affecting Reactivity of Cl-F Bonds. Several significant conclusions are possible regarding the reaction of these Cl-F compounds with HNF_2. The relative order of reactivity for the various systems is:

$$ClF_3\text{-}HNF_2 > ClF_5\text{-}HNF_2 > ClF_3\text{-}HNF_2 \cdot BF_3 > ClF_2^{+}BF_4^{-}\text{-}HNF_2 > RbClF_4\text{-}HNF_2$$

The place of $ClF\text{-}HNF_2$ in the series was not established owing to its high reactivity with glass, which precluded following the course of the reaction through increasing vapor pressure as in the other systems. Probably it is as rapid or more so than $ClF_3\text{-}HNF_2$. The place of $KF \cdot KClF_4$ in this series is doubtful, but it is probably comparable to that of $RbClF_4$. It was determined that the predicted Cl-N bond is formed in all cases. The alternative

possible reactions:

$$ClF_3 + HNF_2 \longrightarrow NF_3 + HF + ClF$$

$$ClF_5 + HNF_2 \longrightarrow NF_3 + HF + ClF_3$$

cannot be occurring to any great extent, if at all, since no ClF or ClF_3 was observed in the reaction of ClF_3 or ClF_5, respectively. Very often there was a direct correspondence between the amounts of $ClNF_2$ observed and the loss of Cl-F species. This is consistent with the earlier noted result.

An interhalogen fluoride of reduced reactivity was also studied; the compound chosen was IF_5. The proposed reaction was examined in both the glass and plastic reactors.

$$IF_5 + HNF_2 \not\longrightarrow HF + IF_4NF_2$$

Because of the relatively high temperature (0 C) necessary to melt the IF_5, the reaction was found to give unwanted degradation products, including I_2. In fact, only small amounts of N-F materials could be found.

REACTIONS OF DIFLUORAMINE AND INORGANIC
FLUOROXY COMPOUNDS

The synthesis of inorganic ONF_2 compounds has been attempted by the reaction of difluoramine and the fluoroxy compounds, oxygen difluoride, fluorine nitrate, and fluorine perchlorate. These reactions may be represented by the general equation:

$$XOF + HNF_2 \xrightarrow{KF} XONF_2 + KHF_2$$

where

$X = NO_2$, or ClO_3

The successful utilization of organic hypofluorites in the synthesis of new organic ONF_2 compounds at Rocketdyne was the basis for this approach (Ref. 20). Since the yields of organic reactions appeared to be enhanced by adding N_2F_4, it is likely that the following types of reactions were involved:

$$XOF + HNF_2 \xrightarrow{KF} KHF_2 + XO\cdot + NF_2\cdot$$

The inorganic radical species from such reactions would be $NO_3\cdot$ and $ClO_4\cdot$. Although no reproducible evidence for ONF_2 compounds was observed, the reaction products could be explained by the reaction of $NF_2\cdot$ or N_2F_4 with $NO_3\cdot$ and $ClO_4\cdot$ radicals or their decomposition products.

$$NF_2\cdot + NO_3\cdot \longrightarrow NO_2,\ FNO_2,\ \text{and}\ N_2F_4$$

$$NF_2\cdot + ClO_4\cdot \longrightarrow FNO\ \text{and}\ FClO_3,\ \text{with smaller quantities of}\ N_2F_4\cdot\ FNO_2,\ Cl_2$$

Although the observed products can be most easily explained by assuming the participation of ONF_2 radical species, the absence of NF_3O as a product is a possible deterrent to such a postulate. The absence of N_2F_2, as well, suggests that the NF diradical also is an unlikely participant in the reactions. Noncondensible gases, O_2 or F_2, were also absent in these reaction products.

THE REACTION OF DIFLUORAMINE-ALKALI METAL FLUORIDE COMPLEXES WITH DIFLUORODIAZINE

The basic behavior of cis-N_2F_2 with AsF_5 suggested that a reaction between cis-N_2F_2 and HNF_2 to form HF and $-NF=N-NF_2$ or $NF_2-N=N-NF_2$ may be possible. Accordingly, this reaction was carried out with the $HNF_2 \cdot KF$ complex and the $HNF_2 \cdot CsF$ complex to provide a driving force by the formation of KHF_2 or $CsHF_2$ respectively. The reactants were slowly warmed from -142 C, and were recovered unchanged in the case of potassium fluoride complex. When the volatiles were removed from the $N_2F_2-HNF_2 \cdot CsF$ mixture at -80 C and examined by their infrared spectrum, unknown material giving rise to absorptions at 5.35 μ, 6.2 μ, and 11.0 μ, were found. The peak at 11.0 μ may be due to NF_3, which in itself would indicate some reaction between N_2F_2 and HNF_2. Explosive decomposition of $CsF \cdot HNF_2$ did not occur until near -20 C; therefore temperatures somewhat above -80 C may be investigated.

MISCELLANEOUS REACTIONS

Reaction of NF_3O With BF_2Cl

The reversible dissociation of NF_3OBF_3 complex suggested that some $ClNF_2O$ might be synthesized by dissociation of the NF_3OBF_2Cl or $NF_2O^+BF_3Cl^-$ complex. An equilibrium mixture of boron fluoride chlorides, rich in BF_3 and BF_2Cl, was pumped on at -142 C to remove most of the BF_3. The residual mixture was reacted with NF_3O at -142 C and warmed to -80 C. The products recovered after further warming gave evidence of the following reaction:

$$2NF_3O \cdot BF_2Cl \rightarrow NF_3O + BF_3 + Cl_2 + NOBF_4$$

Whether chlorine resulted from BF_2Cl oxidation or $ClNF_2O$ decomposition could not be determined.

Nuclear Magnetic Resonance Studies of $FNO-ClF_5$ and FNO_2-ClF_5 Mixtures

Slight interactions between FNO and ClF_5 or FNO_2 and ClF_5 were considered possible at low temperatures on the basis of previous evidence (Ref. 21 and 22). The appealing possibility of the low-temperature existence of the anions F_2NO^- and $F_2NO_2^-$ warranted an examination of the $FNO-ClF_5$ systems by F^{19} NMR. Even slight interactions between these moieties should be detectable by this method. A comparison of the chemical shifts and splitting constants of the pure components and their mixtures was made, and no evidence for interaction was found. The data are summarized in Table 3. The assignment of the peak at 95 and 101 ppm to $FClO_2$ was subsequently checked against a pure $FClO_2$ spectrum which had a singlet resonance at 97 ppm at -80 C.

The disparity between the observations above and the reported complexes $FNO \cdot ClF_5$ and $FNO_2 \cdot ClF_5$ is unexpected. One would expect some detectable intermolecular interactions; the fact that we detected no complex is attributed to our observing only the liquid phase in the n.m.r. tube.

Difluoramine-Chloryl Fluoride Reactions

Another approach designed to establish a Cl-N bond from an active Cl-F compound and HNF_2 involved $FClO_2$. This compound has been demonstrated to couple with an acidic hydrogen (Ref. 23):

$$FClO_2 + HOSO_2F \longrightarrow O_2ClOSO_2F + HF$$

TABLE 3

NUCLEAR MAGNETIC RESONANCE SPECTRA OF FNO, FNO_2, ClF_5, $FNO-ClF_5$, AND FNO_2-ClF_5

Components	Chemical Shift Relative to F_2, ppm	J Value, cps	Assignment	Temperature, C
FNO	-60	unresolved		-80
FNO_2	34	116		-59
	36	118		-41
ClF_5	164	142	doublet	-80
	1		quintet	
$FNO-ClF_5$ (1:2)	-62	unresolved	FNO	
	31	130	FNO_2	
	101	singlet	$FClO_2$	-108
	167	145	ClF_5 doublet	
	0		ClF_5 quintet	
FNO_2-ClF_5 (1:1)	31.5	118	FNO_2	
	95	singlet	$FClO_2$	-60
	167.5	130	ClF_5 doublet	
	- 2.5		ClF_5 quintet	
FNO_2-ClF_5 (1:1)	30	123	FNO_2	
	95	singlet	$FClO_2$	-80
	167.5	130	ClF_5 doublet	
	-3.5		ClF_5 quintet	

NOTE: External standard used to calibrate scale $(CF_3CO)_2O$

With HNF_2, the reaction might be expected to proceed as follows:

$$FClO_2 + HNF_2 \not\longrightarrow HF + O_2ClNF_2$$

Since ClO_2 and possibly $FClO_2$ as contaminants have been credited with deflagrations in previous ClF_3-HNF_2 experiments (Ref. 24) the complex $ClO_2^+BF_4^-$ was employed as the reactant.

Chlorine dioxide was removed from the relatively nonvolatile complex at -80 C. The complex was then transferred to the Kel-F reactor, and HNF_2 was added at -142 C. Upon warming the mixture to -80 C, a deflagration occurred.

The gases, noncondensible at -196 C, came almost exclusively from the HNF_2. However, among the condensible products, there was a small amount of unidentified material with a sharp doublet infrared absorption at 7.6 and 7.7 microns. This does not correspond to $FClO_2$, ClO_2, or $FClO_3$ absorptions, and may indicate the desired compound. Unfortunately, the N-F region was obscured by the presence of NF_3, and the sample was too small to purify. Nearly all the $FClO_2$-BF_3 complex was recovered. It is likely that the deflagration was caused by ClO_2 which was formed during transfer of the complex into the reactor. Experiments in which both the $FClO_2$ and HNF_2 are complexed with BF_3 have eliminated deflagrations, but the desired compound has not been prepared. The HNF_2 was converted to $NOBF_4$.

The Fluorination of BrF_5

Since the high-pressure, high-temperature fluorination of $CsBrF_6$ and BrF_5 has been unsuccessful (Ref. 29), a low-temperature reaction with a discharge-excited fluorine stream was attempted. When the frozen products were warmed, no noncondensibles were observed. Similar negative results were obtained when a stream of premixed BrF_5 and excess F_2 was passed through a glow discharge and immediately frozen.

Fluorination of FNO

A room-temperature reaction of FNO and ClF_3 was conducted, and, in addition to the products FNO_2, $FClO_2$, ClO_2, and unreacted ClF_3, an unknown was also observed in the infrared spectrum of the products. The unidentified material had infrared absorption peaks at 5.8 μ (doublet), 7.2 μ (broad), 8.4 μ (singlet) and 9.7 μ (PQR). This reaction will be re-examined.

EXPERIMENTAL DETAILS

PREPARATION OF Cl_2O

Chlorine monoxide was prepared in high purity from the reaction of chlorine gas diluted with nitrogen, and dry, freshly prepared yellow mercuric oxide (Ref. 25)

$$2Cl_2 + (n+1)HgO \longrightarrow Cl_2O + HgCl_2 \cdot nHgO$$

The Cl_2O was stored in Pyrex ampoules at -196 C.

ALKALI METAL FLUORIDES

To ensure dry potassium fluoride and cesium fluoride, both compounds are first fused, and then powdered and handled in a dry box.

PREPARATION OF FLUORINE NITRATE

Fluorine nitrate was prepared by the reaction of F_2 on dried $NaNO_3$ (Ref. 26)

$$NaNO_3(s) + F_2(g) \longrightarrow FNO_3(g) + NaF(s)$$

The FNO_3 was stored at ambient temperature in a stainless steel cylinder.

PREPARATION OF HNF_2

Difluoramine was prepared by the aqueous fluorination of urea followed by the treatment of the fluorinated urea solution with concentrated H_2SO_4.

The impure HNF_2 was purified by low-temperature fractionation, and was stored in glass ampoules at ambient temperature.

FLUORINATION REACTIONS

Over 20 reactions of the fluorination of Cl_2O over CsF at -80 C have been carried out. Typical experiments utilize 5-millimole quantities of material. The fluorinations were carried out using a 300-milliliter, stainless steel, high-pressure, Hoke cylinder fitted with a high-pressure Hoke needle valve (Y 3002 H). The Cl_2O was condensed into the cylinder from a metal high-vacuum system. The desired amount of fluorine was then condensed into the cylinder at -196 C. The cylinder was then warmed to the desired reaction temperature, usually -80 C. Solid starting material was handled in the dry box. Fractionation of the products was carried out in a metal vacuum system equipped with Teflon traps. The purification of oxychlorine trifluoride is readily accomplished in the vacuum line by trapping at -95 C. Identification of reaction products was by infrared analysis, using an infrared cell constructed of stainless steel and equipped with AgCl windows.

PREPARATION OF FLUORINE PERCHLORATE

Fluorine perchlorate was prepared by passing fluorine at 1 atm through 70 percent perchloric acid at 0 C in a Kel-F U-tube. Gas-liquid contact was increased by packing the U-tube with high-surface, inert, 12-mesh, aluminum oxide. The gas stream was passed through traps at -142 C and -196 C and then through a Fluorolube oil bubbler before venting over ammonia. The products in the -142 C trap were 60 percent fluorine

perchlorate and 40 percent perchloryl fluoride. Three similar preparations proceeded without incident, including subsequent purification, warming, and transfer of the fluorine perchlorate. The fluorine perchlorate was identified by its infrared spectrum.

DIFLUORAMINE-FLUORINE PERCHLORATE REACTIONS

The reaction of difluoramine and fluorine perchlorate was carried out by warming the reactants in stainless steel from -152 C to room temperature. The reaction proceeded smoothly on the basis of observed gradual pressure changes. The reaction products were $FClO_3$, FNO, and smaller amounts of FNO_2, N_2F_4, and Cl_2. Some unreacted $FOClO_3$ was recovered. The primary products, FNO and $FClO_3$, were presumed to arise from the reorganization of NF_2 and ClO_4 radicals. When KF was added to difluoramine before the introduction of fluorine perchlorate, an explosion occurred upon warming the reactants above -80 C

REACTION OF CHLORINE TRIFLUORIDE AND DIFLUORAMINE

A reactor made of Kel-F and fitted with a Teflon valve was used for the reactions; into it was condensed chlorine trifluoride (8.1 cc, 0.362 mmoles) at -196 C. The valve was then closed and the reactor was connected to the glass vacuum line from which the difluoramine (24.2 cc, 1.07 mmoles) was condensed into the reactor at -142 C The reactor was then closed again and the cooling bath changed to -78 C. After 30 minutes, the reactor was opened and fractionated on the metal high vacuum system. An infrared spectrum of the material in the -142 C fraction showed the absence of any Cl-F or N-F species, and indicated that HF

was the only absorbing compound present. Similar inspection of the -196 C fraction (16.2 cc) revealed that it consisted of 1 percent or less NF_3, the remainder being a 1:1 mixture of $ClNF_2$ and N_2F_4. Thus the reaction of ClF_3 and HNF_2 was complete and nearly quantitative.

REACTION OF CHLORINE MONOFLUORIDE AND DIFLUORAMINE

After carefully passivating the Kel-F reactor with ClF_3, it was evacuated and attached to the glass vacuum line. Difluoramine (32.1 cc, 1.43 mmoles) was condensed in at -142 C. The closed reactor was then reattached to the metal vacuum line and ClF condensed in at -142 C, the quantity (32.0 cc, 1.44 mmoles) being measured by pressure difference since ClF has a small vapor pressure at this temperature. After 30 minutes at -78 C, the product gases were separated by fractional condensation at -142 C and -196 C. The high-temperature fraction was found to be HF without any infrared-observable contaminants. The low-temperature sample (31.9 cc, 99.4 percent) did not contain any unreacted ClF, but was composed of a mixture of 97 percent $ClNF_2$ and 3 percent N_2F_4. The latter may have arisen through incomplete reaction of the difluoramine and its subsequent decomposition in the metal line during fractionation.

REACTION OF CHLORINE MONOFLUORIDE AND TETRAFLUOROHYDRAZINE

Equal volumes (22.4 cc, 1.0 mmole) of ClF and N_2F_4 were condensed into a Teflon U-trap incorporated into the metal vacuum system. After standing at -78 C for 30 minutes, the mixture was allowed to expand at ambient temperature (44.8 cc, 100 percent recovery) and an infrared sample was taken. It was observed that some slight decomposition of the N_2F_4 had

occurred, giving FNO and FNO_2. This may have been due to a minute air leak. However, the N_2F_4 recovery represented 92 to 94 percent of the starting material, and no indication of any NF_3 or $ClNF_2$ was present. The ClF which was also present could not be accurately measured due to overlap of its absorptions and those of FNO. Nevertheless, no reaction of ClF and N_2F_4 under these conditions was found.

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The new oxidizer oxychlorine trifluoride, ClF_3O, has been prepared in high yields by the fluorination of Cl_2O. Preliminary results indicate this new oxidizer boils at 30 ±5 C. Concomitant with the formation of ClF_3O, it was found that Cl_2O is acidic to CsF inasmuch as complexes of the type $CsF \cdot Cl_2O$ are formed. This material represents a new class of compounds. The preparation of ClF_3O was attempted by a variety of routes. Metathetical reactions of ClF_5 did not yield ClF_3O nor did the careful hydrolysis of ClF_5 give rise to ClF_3O. The fluorination of commercial calcium hypochlorite gave inconclusive results. Discharge reactions of F_2 with Cl_2O and ClO_2 gave no new species; nor did the discharge reaction of O_2 with ClF_3 and ClF_5 give rise to new compounds. The preparation of Br_2O was accomplished for study with F_2 and CsF. The compound (IF_3O), was found to be best represented by the composition $IO_2^+IF_6^-$. Using HNF_2 and ClF_3 in a variety of forms failed to yield ClF_2NF_2. The stoichiometry of the reaction was found to follow the equation $ClF_3 + 3HNF_2 \rightarrow ClNF_2 + N_2F_4 + 3HF$. It was also found that the action of ClF on HNF_2 gave a quantitative yield of $ClNF_2$ and represents a new preparation of $ClNF_2$. The reaction of NF_3O and BF_2Cl failed to give NF_2ClO. The F^{19} n.m.r. examination of the systems FNO-ClF_5 and FNO_2-ClF_5 showed no interaction in the liquid state. (Confidential Abstract)

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